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EVALUATION OF SOME WIDE-DYNAMIC-RANGE READOUT SYSTEMS FOR PHOTOELECTRIC INTEGRATING SPECTROMETERS

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16. Abstract

Five types of electronic circuits commonly used for readout of currents from photomultiplier tubes were evaluated. This evaluation was conducted to define the experimental limits of achieving the widest possible dynamic range of light detection and concentration measurements in spectrochemical analysis. The circuits evaluated included the photon-counting technique and four dc circuits. These circuits displayed a dynamic range from 3 to about 4.5 decades within a repeatability criterion of 1 percent, or better. The maximum dynamic range allowed by the photomultiplier tube in this application was estimated to be about 6 decades.

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SUMMARY

Five types of electronic circuits commonly used for readout of photomultiplier currents in photometric instruments were evaluated to define the experimental limits in achieving the widest possible dynamic range of light detection for wide-range concentration measurements in emission spectrochemical analysis. In keeping with the precision requirements for this application, dynamic range was defined as the range of photocurrents giving repeatabilities of 1 percent, or better. By this definition, strict linearity of the readout was not required.

The circuits examined included the photon-counting technique and four dc circuits. All the dc circuits, in varying configurations, used a capacitor to integrate the photocurrents and a high-input-impedance operational amplifier as an interface between the photomultiplier tubes and the final readout display.

The dynamic range of the photon-counting circuit was about 4.5 decades with operational conditions typical in emission spectroscopy. This circuit was limited on the low end by shot noise and detector noise, and on the high end by the frequency response of the amplifier-discriminator. The dynamic range of the analog circuits was from 3 to 4.5 decades and was limited on the low end by ambient electrical noise and on the high end by the maximum voltage rating of currently available operational amplifiers. The maximum dynamic range allowed by the photomultipliers typically used in this application was about 6 decades, as estimated from manufacturers' specifications.

A discussion is also given of some other considerations, in addition to dynamic range, when these circuits are used in multichannel photoelectric spectrometers.

INTRODUCTION

In the determination of chemical composition by optical emission spectroscopy, it is desirable to analyze the widest range of concentrations in a single sample and with a

single spectral line. The maximum dynamic concentration range determinable with a single spectral line is inherently limited by the emission characteristics of the plasma used to excite atomic spectra. At the low-concentration end the range is limited by the background intensity fluctuations, or noise, inherent in every plasma. The high-intensity-range limit is imposed by either or both of two factors: (1) self-absorption of radiation in the emission plasma, and (2) line broadening in excess of the exit slit width of the spectrometer. The development of excitation sources allowing determinations over a wide concentration range is a fundamental problem in emission spectroscopy. However, with the development of sources with wide dynamic range, the development of readout systems with commensurate dynamic range is also necessary.

Recent refinements of the direct-current arc excitation source at the Lewis Research Center (ref. 1) have resulted in useful ranges of analysis of more than 3 decades (1000). This dynamic range exceeds the capabilities of readout systems on commercially available photoelectric spectrometers, which are limited to about 2 decades with achievable precisions of at least 1 percent. An example of the limitation imposed by the readout system at the Lewis Research Center is shown in figure 1. This plot shows the response of the readout system as a function of the amount of titanium in the samples and also as a function of increasing exposures to a constant light intensity. The concentration curve for titanium is typical of some 20 other elements also programmed for analysis in the spectrometer. The curve showing response to an increasing exposure to

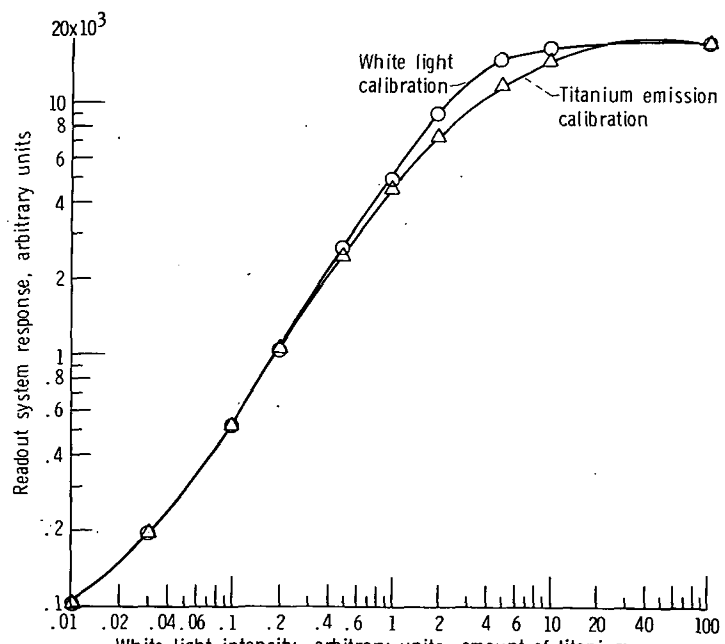


Figure 1. - Example of limitation imposed by readout system on dynamic range of spectrochemical analysis.

a constant light intensity represents the maximum useful range of the readout system. Comparison of these response curves shows that most, but not all, of the nonlinearity at higher titanium concentrations is attributable to the readout system. Therefore, it is apparent from figure 1 that increasing the dynamic range of the readout system is necessary to extend the higher range of concentrations determinable by this method.

This report contains the results of evaluation of five circuits applicable to integrating photoelectric spectrometers, with special consideration given to the requirement of wide dynamic range. The evaluation was conducted to define the limits in achieving wide dynamic range with these circuits and generally to assess the suitability of these circuits for readout of photocurrents in spectrochemical analysis. A discussion is given of some basic considerations of each readout circuit when it is used in this application.

DEFINITIONS OF DYNAMIC RANGE

The definition of dynamic range is often stated in terms of the resolution element of the system. For example, a device with a resolution of 1 part in 10 000 is said to have a dynamic range of 10 000, or 4 decades. However, in the context of this work, the term dynamic range is intended to apply to a practical analysis system and is defined in terms of the concentration resolution. Therefore, the definition of dynamic range in this work is the span over which precisions of 1 percent (relative standard deviation), or better, are achieved without range changing. This precision represents a maximum allowable error due to the readout system alone and is acceptable for even the most stringent analytical requirements. By this definition, a resolution of 1 part in 10 000 is said to have a dynamic range of 2 decades within the 1 percent limit because readout of at least 100 parts is required to ensure a precision of 1 percent. Definitions of dynamic range, of course, can be made in terms of any arbitrary precision limit. It should also be recognized that the precision limit can logically be defined as a function of concentration to reflect the wider limits of acceptable precision in the trace concentration range compared with the major constituent ranges. However, the results and conclusions of this work are not dependent on the precision criterion selected, except in the case of the photon-counting circuit as discussed in the section Photon Counting - Circuit V.

In defining dynamic range, the absolute linearity was not of primary importance. Good linearity of a readout device is a primary consideration when the readout data are reduced manually and experimenter bias may produce errors in reading concentrations from scales or graphs. With modern digital data processing the linearity requirement is secondary due to computer interpolation accuracy. All that is required when computer processing of data is used is that the resolution elements in terms of concentration

be within specified limits. Therefore, special efforts to make the readout precisely linear are not justified if the concentration resolution can be achieved.

APPARATUS AND PROCEDURE

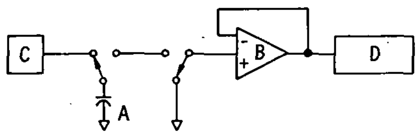
The five circuits that were investigated for application to readout of photocurrents from a photoelectric spectrometer are shown schematically in figure 2. The components in these circuits which are critical in this application include the integrating capacitors, the field-effect-transistor operational amplifier (FET-OA), and the digital voltmeter. These components are common to all the circuits except circuit V, the photon-counting circuit. The specifications of these components which are important in this application are summarized in table I.

Circuit I

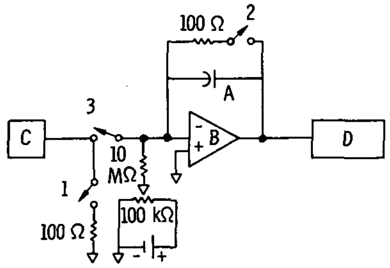
In circuit I (fig. 2(a)) the capacitor was connected between the anode and the ground of the photomultiplier (PM) tube. After integration, the voltage on the capacitor was measured directly by switching the charged capacitor to the FET-OA connected as a voltage follower. This system presents an impedance of about 10^{11} ohms to the charge on the capacitor and therefore permits voltage readings without significant discharge of the capacitor. The voltage at the output of the OA was measured with a $4\frac{1}{2}$-digit voltmeter.

To test this circuit, a 0.1-microfarad capacitor was used for integration of the known input currents. The capacitor was charged to an accurately known voltage and then connected to the readout bus, which in multichannel operation would sequentially connect each channel capacitor to the input of the OA. The mercury-wetted reed relay was used to provide bounceless switching in connecting the input to the OA to ground. Five milliseconds after the charged capacitor was switched to the OA input, the auto-ranging digital voltmeter was given a digitizing command. The relative standard deviations were calculated for at least 10 repeat readings in the voltage range between 1 millivolt and 100 volts, and these data were used to determine the dynamic range of the system.

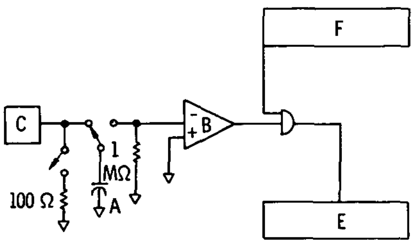
A Integrating capacitor, 0.1 μF
B Operational amplifier
C Photomultiplier tube
D Digital voltmeter
E Digital counter
F Oscillator
G Monostable multivibrator
H Pulse height discriminator
I Decade counting unit



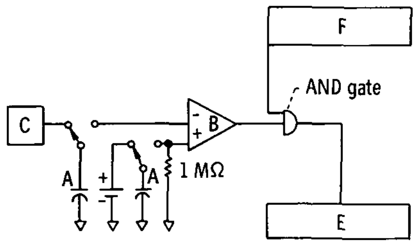
(a) Direct capacitor voltage - circuit I.



(b) Integrating amplifier - circuit II.

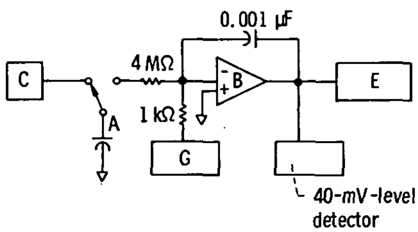


Circuit III(a)

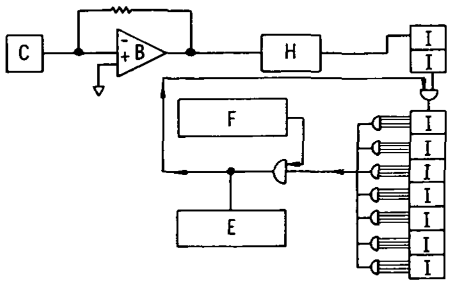


Circuit III(b)

(c) Time of capacitor discharge - circuits III(a) and III(b).



(d) Voltage-to-frequency converter - circuit IV.



(e) Photon-counting - circuit V.

Figure 2. - Schematic circuits of readout systems evaluated.

TABLE I. - COMPONENT SPECIFICATIONS

Component	Specifications	Used in-
Capacitors	Type, polystyrene (hermetically sealed) Resistance, 10^{14} Ω/F	Circuits I, III(a), III(b), and IV
Operational amplifiers	Type, field-effect transistor Limit voltage, 100 V Power supply, 115 V; 0.1 percent regulation for 10-percent change in load Input bias current, 50 pA (max); temperature coefficient, doubles for 10° C rise Input voltage offset, 1.0 mV adjustable to zero; temperature coefficient, 30 μV per C°	Circuits I, II, III(a), III(b), IV, and V
Digital voltmeter	Direct-current ranges: 10 mV, 100 mV, 1 V, 10 V, 100 V, and 750 V (autoranging) Sensitivity, 1 μV on 10-mV range Digitization time, 0.5 sec	Circuits I and II
Photomultiplier tubes	Type, Radio Corporation of America 1P28 and 1P21 Supply voltage (typical), 800 V Maximum anode current, 500 mA Anode dark current, (typical) $2{\times}10^{-10}$A Current amplification, $6{\times}10^{5}$ electrons per photon	All circuits
Amplifier discriminator	Voltage gain, 2500 V Bandwidth, 10 kHz to 250 MHz Maximum counting rate, 25 MHz; discriminator level, 50 mV; pulse-pair resolution, 10 nsec	Circuit V

Circuit II

This circuit provides true integration of photocurrents because the capacitor is in

the feedback loop of an OA. In the circuit shown in figure 2(b), the OA summing point was initially connected to ground through the 100-ohm resistor with a 100-ohm resistor in the feedback loop for balancing voltage offset. During integration of the photocurrent, reed relays 1 and 2 were open. After an accurately timed integration, relay 3 opened and relay 1 closed. This stopped the integration and held the voltage until readout by the digital voltmeter. The digitization was commenced immediately after switching the capacitor from the PM tube. After digitization, the capacitor was discharged into the 100-ohm resistor by closing relay 2. A variable voltage source of ±1.0 volt and a 10-megohm resistor provided a method of bucking the dark current and the spectral background current by summing at the OA input. Repeatability readings were taken over a voltage range from 100 volts to 1 millivolt.

Circuits III(a) and III(b)

In circuit III(a) of figure 2(c), a capacitor was again used to integrate the photocurrent. The stored charge was measured by determining the time required to discharge the capacitor through a fixed resistor to some threshold voltage level.

The repeatability test for this circuit consisted of charging the capacitor to accurately known voltages. The capacitor was then switched to the discharge resistor by a mercury-wetted relay connected between the inverting input of the OA and ground. The output of the OA slewed from the negative limit to the positive limit, where it remained until the capacitor voltage discharged to the preset discriminator level, whereupon it slewed back to the negative limit. The noninverting input of the OA was grounded and the voltage offset potentiometer was adjusted for minimum offset without oscillation. This offset voltage was 30 millivolts, at which level the discriminator was set. The output of the OA was fed directly into a digital counter with a 1-megohm input impedance. The counter displayed six digits and was set in the period mode and driven by a 1-megahertz oscillator. This enabled the pulse from the OA to be measured to ±1 microsecond. Repeatability checks were made by using a 1-megohm discharge resistor in the voltage range from 100 volts to 50 millivolts. Because of the discharge characteristic of capacitors, the output digital data were proportional to the natural logarithm of the capacitor voltage (time = k ln V).

In circuit III(b) (fig. 2(c)), a variation of circuit III(a), a reference capacitor was discharged through a fixed resistor until its voltage equaled the voltage on the analysis capacitor. The analysis capacitor was charged by photocurrents to be measured, as in circuit III(a), whereas the reference capacitor was charged by a constant voltage source. The reference capacitor was charged to the highest voltage that would ever be expected to occur on the analysis capacitor. After charging, both capacitors were switched to

the OA inputs. The time required to reach an equilibrium voltage on the discharge resistor was inversely proportional to the natural logarithm of the voltage on the analysis capacitor (time = $K(1/\ln V)$).

This circuit was checked for repeatability by switching the positive high-impedance input from ground to the integrating capacitor. This kept the OA output at the negative voltage limit. Next, the charged reference capacitor was switched by a bounceless mercury-wetted reed relay to the 1-megohm discharge resistor connected to the inverting input. The OA output then slewed to the positive limit, where it remained until the two capacitor voltages were equal. At that time the OA output went to the negative limit. The duration of the output pulse from the OA was measured within 1 microsecond by the digital counter used in circuit III(a).

Circuit IV

Circuit IV (fig. 2(d)) digitized the total charge on the integrating capacitor in small charge increments. The integrating capacitor, initially charged with photocurrent, was switched to the OA input through a 4-megohm resistor. The OA integrated the current from the integrating capacitor until the OA reached 40 millivolts, the voltage detector level. This caused voltage of opposite polarity to be applied for a fixed time pulse through a 10-kilohm resistor to the OA summing point by a monostable multivibrator. This, in turn, caused the output of the OA to integrate negatively, which discharged the capacitor in the feedback loop. The output pulses, resulting from periodic reset operations, were accumulated for 2 seconds on the counter.

Repeatability tests were made by applying accurately known voltages, between 100 millivolts and about 100 volts, to the integrating capacitors.

Circuit V

The photon-counting circuit shown schematically in figure 2 was evaluated from experiments conducted with less than state-of-the-art electronic components and by extrapolating these results using specifications of the best components currently available.

In the circuit of figure 2 the amplifier-discriminator specification, in particular, is crucial for achieving the maximum dynamic range. Typical specifications for a state-of-the-art amplifier-discriminator are as follows: voltage gain, 2500 volts; bandwidth, 10 kilohertz to 250 megahertz; maximum counting rate, 25 megahertz; discriminator level, 50 millivolts; and pulse-air resolution, 10 nanoseconds.

In multichannel operation, a seven-decimal-digit high-speed counter is required for each channel to record the 25-megahertz signal for 10 seconds. Alternatively, the counts can be stored on decade counting units (DCU) as illustrated in figure 2(e), and sequentially displayed on the counter. It is not necessary to decode the first two decade counting units since they are not significant within the 1-percent precision criterion. By decoding only the highest seven digits and injecting 10-megahertz readout pulses at the third DCU, the decoding time was only 1.0 second, whereas it would be 100 seconds per channel for nine decimal digits.

The dynamic range of this circuit was estimated by using the relations between precision and number of photon events expressed by

$$N = \frac{1}{\epsilon G} \int_0^t i \, dt \tag{1}$$

where

N	number of photon events
ϵ	electron charge, 1.6×10^{-19} C/electron
G	gain of photomultiplier tube, electron per photon
$\int_0^t i \, dt$	current integral, A-sec

and

$$s = \left(R_{S+B} + 2R_B\right)^{1/2} t^{1/2} \tag{2}$$

where

s	standard deviation
R_{S+B}	count rate of signal plus background
R_B	count rate of background
t	integration time

as given in reference 2.

RESULTS AND DISCUSSION

The dynamic range of the various circuits evaluated is summarized in figure 3 in the form of error curves as a function of photocurrent. These curves were either calculated or experimental as indicated in the figure. The dynamic range for each circuit at the level of 1-percent precision is indicated by the intercept of the dashed horizontal line with the respective error curves.

The current scale of figure 3 is approximately proportional to analytical concentrations. In practical analysis, the concentration range of interest can be made to correspond to any arbitrary current range within the limits of the spectral line intensities and the photodetectors. This is done, for example, by selection of spectral lines, by sample size, and by adjusting the gains of the photomultiplier tubes. In this discussion, the limitations of the spectral line emissions are not considered, and only the dynamic range of the readout system is evaluated in terms of output current of the PM (photomultiplier) tubes.

Several fundamental limits are presented in figure 3. The maximum photocurrent was taken to be about 5×10^{-4} ampere. This is a typical design limit for a side-window, nine-stage PM tube such as the RCA (Radio Corporation of America) type 1P28. Also shown in figure 3 is an absolute lower limit of attainable precision as a function of photocurrent. This limit was calculated from photon event statistics by using equation (1) and the noise-free precision limit expressed by $\sigma = N^{1/2}$, where σ is the standard deviation and N is the number of photon events. Since this equation is applicable to a noise-free system, it expresses the absolute lower limit of precision attainable in any real system, given the current, the PM tube amplification, and the integrating time. For the calculations of figure 3, G was taken as 6×10^5 electrons per photon, typical of the RCA 1P28 tube with 800 volts applied. All calculations were made for an integrating time of 10 seconds, which is about the minimum integration time in spectrochemical analysis, but which may extend to about 100 seconds in some applications.

From the standpoint of dynamic range alone, each of the circuits would be satisfactory for the great majority of spectrochemical analyses. However, there are significant differences among the circuits for applications where the maximum dynamic range is required. These applications often involve so-called universal procedures which are designed to analyze wide concentration ranges. Some of the important characteristics of the circuits, in addition to dynamic range, are discussed in the following sections.

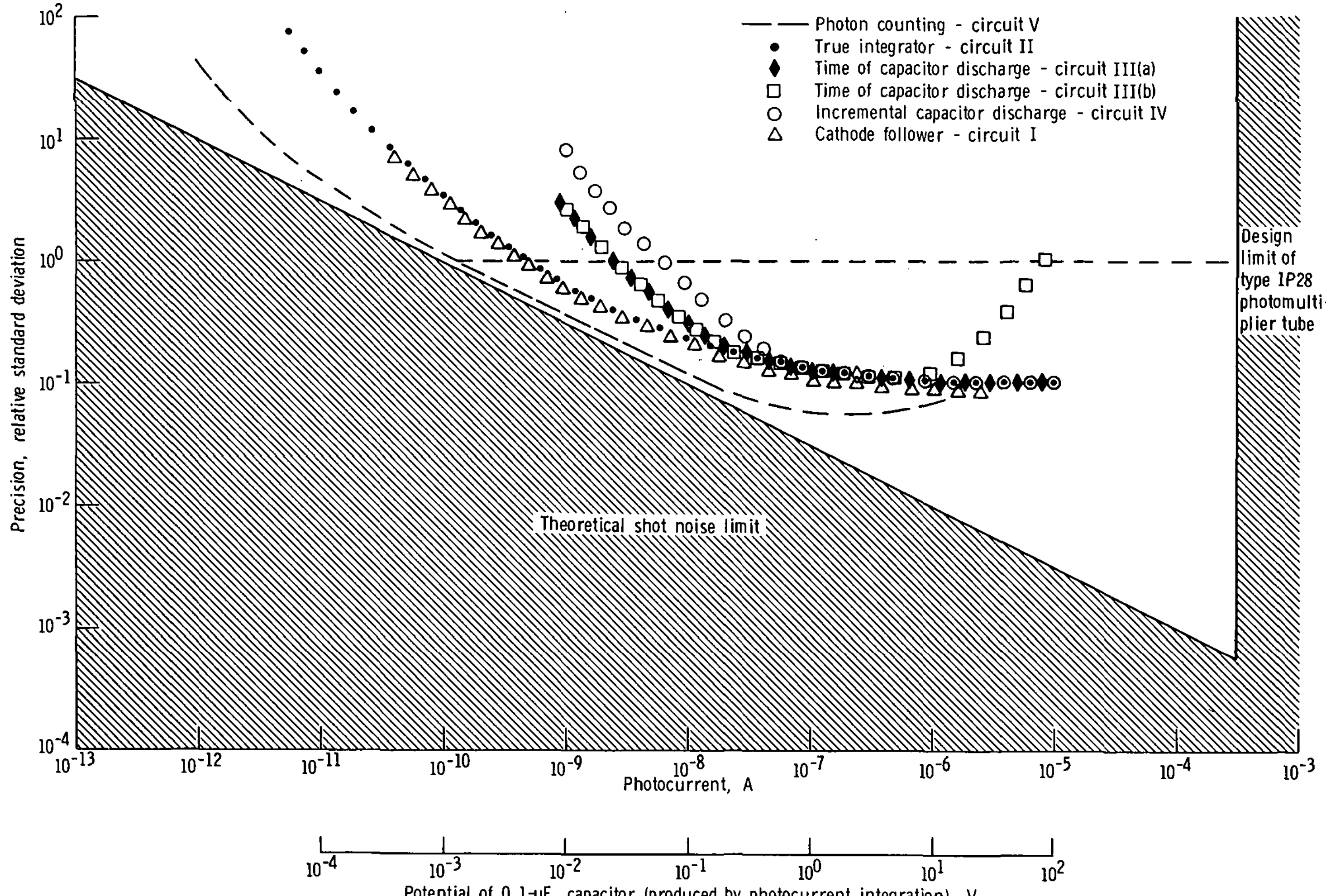


Figure 3. - Precision curves as function of photocurrent and integrating capitor voltage for spectrometric readout systems. Shot noise limit calculated for integration time of 10 seconds, photomultiplier tube gain of 6×10^5 electrons per photon, and photomultiplier tube voltage of approximately 800 volts.

Principle of Operation of Photomultiplier Tubes

To understand how the various readout systems operate and the relative merits of each, it is necessary to discuss some fundamentals of PM tube operation. Figure 4 is a schematic diagram of a typical tube used in multichannel emission spectrometers. The photocathode is normally operated at a high negative potential, between 600 and 1000 volts. A series string of resistors divides the voltage between nine dynodes and ground. The photoelectrons emitted when the photocathode is illuminated are electrostatically focused onto the first dynode and multiplied through the successive nine dynode stages. The photomultiplier, therefore, is a current source which produces an output current proportional to light intensity input. The electron multiplication (gain) of the tube is critically dependent on the voltage between the dynodes. As a general rule, the dynode voltage should be 10 times more stable than the desired output stability (ref. 3). For example, if 0.1-percent stability is desired at the output signal, the voltage applied to the dynode resistors must be regulated to 0.01 percent. These resistors must be chosen so that at least 10 times more current flows through them than is measured as photocurrent (ref. 3). If more than about 10 percent of the dynode current flows through the readout device, the voltage loading between the last dynode and ground is redistributed among the other stages and can cause an increase in photomul-

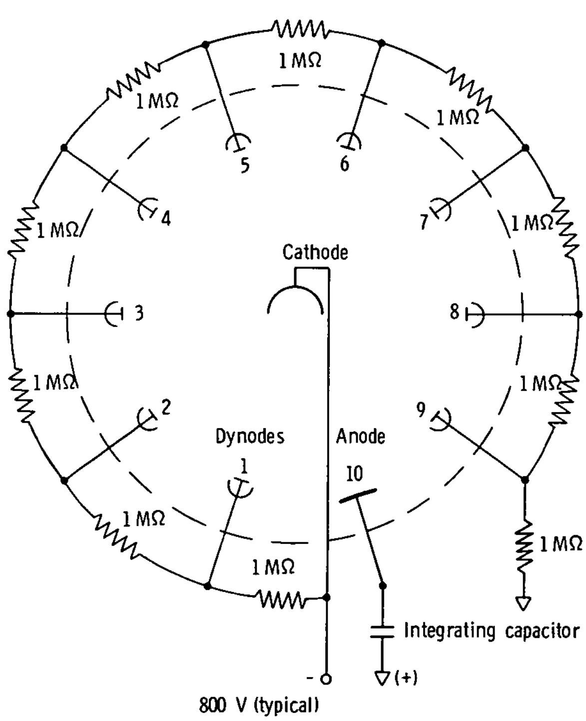


Figure 4. - Schematic of photomultiplier tube with dynode resistor chain and integrating capacitor.

tiplier gain (refs. 3 and 4). For a 10-percent loading of the last dynode there is an approximate 1-percent increase in the voltages between the various stages with an approximate increase of 10 percent in photocurrent. Furthermore, the gain of the first stage has a greater effect on the shot noise than succeeding stages; and this voltage is, therefore, somewhat more critical. Voltage regulator tubes and Zener diodes can be used to fix the dynode voltages, but this approach was not investigated in this work.

When operating voltage is applied to a PM tube, an ohmic leakage current flows even when the tube is in the dark. In addition to this dark current, thermionic noise and pulses due to radioactive background are also present (ref. 2). This dark current is relatively constant and can be subtracted when measuring light intensities.

Storage of Photocurrents on a Capacitor

In all the circuits except circuit V, a capacitor with low leakage specification is used as the charge storage device. In circuit II, the capacitor is effectively buffered from the PM tube anode by the high-impedance OA and can, therefore, integrate current linearly up to the voltage rating of the OA. However, in circuits I, III(a), and III(b) the charging characteristic of the capacitor is dependent on the applied tube voltage, specifically on the last dynode-to-ground potential. Figure 5 shows the charging curve as a

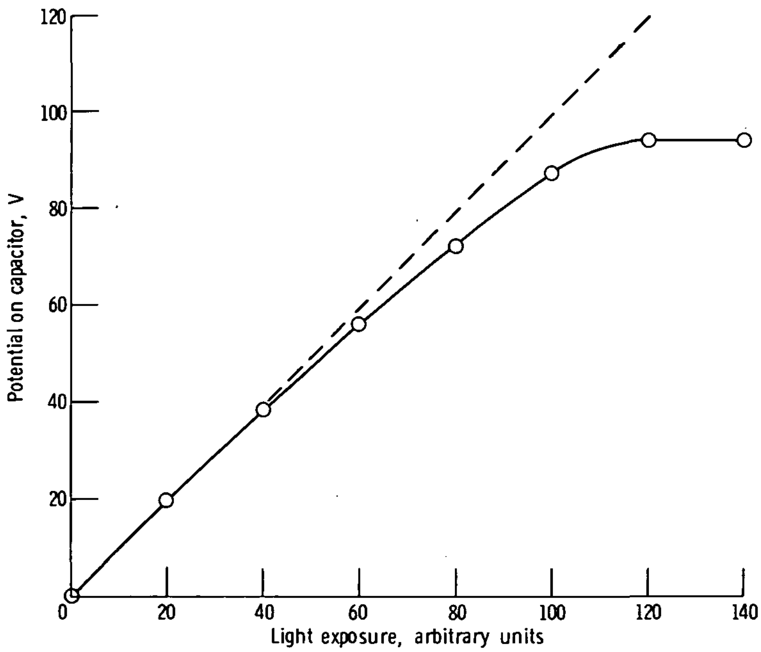


Figure 5. - Potential on integrating capacitor as function of light exposure. Integrating capacitor connected directly to anode of photomultiplier tube which was at potential of -94 volts.

function of time with constant light flux input. The departure from linearity at the high capacitor voltages is the result of decreased anode photocurrent collection. This decrease is caused by the reduction in anode-to-last-dynode voltage as the voltage of the charging capacitor increases. As this difference in potential approaches zero the charging rate is decreased until the capacitor voltage equals the voltage on the last dynode, at which point the capacitor stops charging. Therefore, the maximum voltage to which the capacitor can charge is a function of the applied tube voltage. This places a definite limit of about 60 to 90 volts on the upper voltage range. This is the limiting characteristic of these circuits wherein the capacitor is connected directly to the anode.

Direct Capacitor Voltage - Circuit I

The voltage on the charged capacitor can be measured by using an operational amplifier with an input impedance of 10^{11} ohms, or greater. This circuit yielded a dynamic range of nearly 4 decades with a relative standard deviation of 1 percent, or better. The linearity obtained was as shown in figure 5, because the capacitor was connected directly to the PM tube anode. The nonlinearity is an inherent characteristic of this circuit, as described in the previous section, but is not necessarily a disadvantage with modern curve-fitting techniques and computer processing.

Integrating Operational Amplifier - Circuit II

This circuit gave the widest dynamic range of the analog circuits - about 4.5 decades at 1 percent precision and an additional decade within about 10 percent precision. The dynamic range was limited by environmental noise at a voltage resolution of about 0.1 millivolt, as with circuit I, and by the maximum output voltage of the OA of 115 volts. The capacitor was charged very linearly up to this 115-volt limit and was independent of the voltage on the last dynode. This circuit also has the advantage that bucking currents can be easily applied at the summing point of the OA to compensate for dark currents and spectral background currents.

A disadvantage of this circuit is that a small bias current is required to operate the OA, and this current will either add to or subtract from the photocurrent stored on the capacitor. When the PM tube is disconnected from the measuring circuit prior to readout, this bias current will slowly change the voltage on the capacitor at a rate of about 0.1 millivolt per second for the components specified for this circuit. This corresponds to a bias current of about 10 picoamperes. The manufacturer's specification on the OA's used was 50 picoamperes.

The bias current of the OA is very constant and does not significantly affect the repeatability of measurements if the timing sequences of the readout are also highly repeatable. In a multichannel spectrometer, the time between disconnect from the PM tube and readout can be up to about 10 seconds for the last channels recorded. In this time the capacitor voltage can change about 1 millivolt, typically. Furthermore, this time was variable in the system tested because of variable delays due to range changing of the autoranging digital voltmeter. When this variable timing sequence can be shown to be a significant source of error, the timing sequence must be slowed to allow for the maximum range-changing delay for each channel recorded. No further definition of this source of error was made in this investigation. Another disadvantage of this circuit is that the cost per channel is somewhat greater than the other analog circuits because a separate high-voltage OA is required for each channel.

Timing of Capacitor Discharge - Circuits III(a) and III(b)

The integrated photocurrents stored on capacitors can be measured by discharging the capacitor through a fixed resistor and determining the time of discharge (ref. 5). The dynamic range of this system was about 3 decades, as shown in figure 3.

The maximum voltage that was measured with this circuit was limited by the maximum voltage appearing at the last dynode of the PM tube, as explained previously, typically between 70 and 90 volts. The discharge of the voltage on the capacitor was timed with a 1-megahertz counter, which allowed sufficient resolution for 4 decades of dynamic range within the precision limit of 1 percent. The time of discharge is proportional to the natural log of the charge on the capacitor

$$T = RC \ln \frac{V_1}{V_2} \tag{3}$$

where

T time of discharge, sec

R circuit resistance, ohm

C analysis capacitor, F

V_1 potential on analysis capacitor, V

V_2 terminal potential on analysis capacitor, V

The lowest voltage that could be detected with this circuit was about 50 millivolts. Below this terminal potential the system was susceptible to ambient noise spikes which caused uncertainties in terminating the timing of the discharge and also tended to start oscillations in the high-gain wide-bandwidth FET-OA. Thus, voltages between about 70 volts and 50 millivolts could be digitized with repeatabilities of 1 percent, or better.

Circuit III(b) was a variation of the time-of-discharge method described previously. In this circuit, the voltage of the analysis capacitor was made relative to the discharge of a reference capacitor voltage. The reference capacitor was charged to some fixed voltage greater than the maximum voltage expected on the analysis capacitor, which was charged with photocurrent. The reference capacitor was discharged through a fixed resistance until the OA input voltages were equal. The time required for voltage equilibrium was inversely proportional to the natural log of the voltage in the analysis capacitor

$$T = RC_2 \ln \frac{V_2}{V_1} \tag{4}$$

where

T time of voltage equilibrium ($V_1 = V_2$), sec

R circuit resistance, ohm

C analysis capacitance, F

V_1 potential on analysis capacitor, V

V_2 potential on reference capacitor, V

Therefore, the larger photocurrents produced the smaller count values. This afforded an approximately constant relative error over the photocurrent dynamic range.

The addition of the reference capacitor in circuit III(b) does not extend the dynamic range, however. Its primary value is in measuring ratios of photocurrents, which is convenient when using internal standards in spectrochemical analysis.

A disadvantage of circuits III(a) and III(b) was that the maximum discharge time was of the order of 1 second per channel. Therefore, these circuits are not compatible with high-speed digital data logging when the maximum dynamic range is required. Furthermore, with circuit III(b) the maximum readout time was required for channels with little or no charge on their respective capacitors. In most applications of multichannel spectrometers, only a few channels contain most of the information. However, with data logging systems with speeds of about 10 to 30 characters per second, these circuits may not be time limiting.

Voltage-to-Frequency Converter - Circuit IV

The dynamic range of a voltage-to-frequency converter circuit, shown in figure 2(d) (circuit IV), was estimated to be about 3.25 decades, allowing a 2-second readout time in the spectrometric application. The dynamic range of this circuit was limited by the speed of the voltage-to-frequency converter. A state-of-the-art converter can operate at a rate of 250 kilohertz with a 0.1-percent nonlinearity, and the voltage-to-frequency converter of figure 2(d) was designed to be compatible with a converter with this frequency response.

In this circuit, the total charge stored on the integrating capacitor was measured by connecting to an integrating-type voltage-to-frequency converter. The counting rate of the converter was proportional to the voltage on the analysis capacitor, which was charged by photocurrent. As the analysis capacitor is discharged through the converter input resistor, its voltage drops exponentially with time until the capacitor is completely discharged, or until the measurement is otherwise terminated. Likewise, the initial count rate of the converter is somewhat higher than the average count rate and falls to zero with complete discharge of the capacitor. With the circuit of figure 2, the initial count rate was about 625 kilohertz, thus exceeding the linear frequency response of the converter. However, the average count rate was 125 kilohertz, and the deviation from linearity resulting from the high initial count rate was acceptable in the interests of maximum dynamic range. The operational amplifier used with this circuit should have a full output capability from -10 volts to +10 volts, at a frequency of 10 megahertz, and low offset current of 50 picoamperes or less.

If the 0.1-microfarad capacitor in circuit IV is charged to a maximum of 100 volts, and with an allowable conversion time of 2 seconds, the voltage-to-frequency converter will produce about 250 000 counts for complete charge transfer (i.e., $C_A V_A / C_f V_{oa} = 250\ 000$, where C_A and C_f are the analysis and feedback capacitors, respectively; and V_A and V_{oa} are the voltages on C_A and the OA output, respectively). In the 2-second allowable conversion time, C_A will discharge to about 0.7 percent of the initial value of V_A. This represents about five time constants of the discharge circuit ($4\ M\Omega \times 0.1\ \mu f$). Therefore, the dynamic range of this system, within the 1-percent repeatability criterion, was between 100 and 250 000 counts, or about 3.25 decades.

A disadvantage of this circuit is that it is not compatible with high-speed data acquisition because of the relatively long readout time required for wide dynamic range. However, it would be suitable for typewriter recording speeds of 10 to 30 characters per second.

Photon Counting - Circuit V

The dynamic range of a state-of-the-art photon-counting system was estimated to be about 4.5 decades, within the 1-percent precision criterion. In figure 3, the dashed portion of the error curve for photon counting was estimated, whereas the solid portion was experimentally verified. The lower limit of the curve was calculated from the shot noise limit for a 10-second integration, a PM tube gain of 6×10^5 electrons per photon, and a PM background of 100 hertz. Each of these values represents typical conditions encountered in spectrochemical analysis. The rate of photon events per ampere of photocurrent was calculated from these conditions by using equation (1). The highest current was estimated to be about 3×10^{-6} ampere as limited by the maximum count rate of the amplifier-discriminator. As this maximum count rate is approached, the amplifier response becomes nonlinear; and as a result the error increases, as indicated in figure 3, but does not exceed 1 percent up to the 25-megahertz cutoff.

The photon-counting technique has some characteristics which make it potentially advantageous as a wide-dynamic-range readout system in emission spectroscopy. Reference 6 presents some of the considerations when using this circuit for spectrochemical analysis. It provides a digital readout for discrete events without an intermediate analog conversion. In addition, the ultimate performance of the system follows well-defined counting statistics according to equations (1) and (2).

However, in addition to the relatively high cost per channel, there are some notable disadvantages of this technique when it is used as a wide-dynamic-range readout system in emission spectrochemical analysis. First, the photocurrents measured are usually in a range where dc circuits perform equally as well or better than photon-counting circuits. As pointed out in references 7 and 8 and other sources, the photon-counting circuit outperforms dc circuits at low light levels which produce photocurrents of the order of dark current (i.e., 10^{-10} A and lower). However, the spectrochemical application is usually not light limited and photocurrents up to 10 to 100 microamperes can be supplied, if necessary.

Second, the photon-counting circuit is susceptible to high-frequency noise from high-voltage sparks used to excite atomic spectra. To achieve the lower current limit shown in figure 3 in the presence of such noise will require careful shielding of electronic components.

Third, the photon emission rates in spectrochemical analysis are not constant with time, as was assumed in setting the upper current limit in the analysis of this circuit, but are variable with both arc and spark excitation. Therefore, the upper limit of the photon-counting circuit, as shown in figure 3, is somewhat overestimated because of this approximation.

CONCLUDING REMARKS

Of the circuits evaluated, the photon-counting circuit and the operational-amplifier integrator circuit gave the widest dynamic range within a 1-percent repeatability criterion. Both circuits responded over about 4.5 decades of input photocurrents without range switching. This dynamic range corresponded to photocurrents between about 10^{-10} and 10^{-5} ampere and to voltages of between 1 millivolt and 100 volts on the integrator capacitor.

The low current limit of the photon-counting circuit was defined by the combined effects of theoretical shot noise limit and detector noise, whereas the upper current was limited by the maximum frequency response of the amplifier-discriminator. With the dc operational-amplifier integrator circuit, the lower voltage limit was defined by environmental electrical noise, whereas the upper voltage limit was defined by the maximum operating voltage of the operational amplifiers. The photon-counting circuit was prohibitively expensive for applications requiring more than a few channels, but further advances in technology could make this circuit the method of choice.

Several other dc circuits can also be used to read out photocurrents, but with some compromise of maximum dynamic range as compared with the other circuits mentioned herein. In particular, the circuit configuration in which capacitors were connected to integrate directly and to store the photocurrents, followed by voltage readout with a voltage-follower circuit, gave a dynamic range response of about 4 decades. This circuit was more economical in multichannel operation because only a single voltage-follower circuit was required for all channels.

The other dc circuits, including time of capacitor discharge and incremental capacitor discharge, were limited in dynamic range to about 3.5 decades but were relatively simple and reliable in operation.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 22, 1971,
134-03.

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